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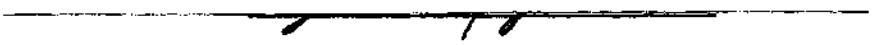

HUMIDITY MEASUREMENT UNDER LOW VACUUM CONDITIONS

A THESIS

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TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF ILLUSTRATIONS

SUMMARY

Four methods for measuring humidity under low vacuum conditions were investigated. These methods involved the use of an electrical hygrometer, a liquid nitrogen cold trap, an ice bulb thermocouple, and a gas analyzer.

The electrical hygrometers used were capable of humidity measurement at low vacuum pressures. These transducers responded to the temperature and the partial pressure of water vapor in their surrounding environment. Three narrow range transducers were used to measure water vapor partial pressures from .3 to 3.2 torr. The calibration curves supplied by the manufacturer were found to be accurate within 5 per cent. This investigation was made for a range of total pressures between .5 and 7 torr. Temperatures between 75F and 85F were considered.

When a liquid nitrogen cold trap was placed in a low vacuum mixture of air and water vapor, the pressure measured across the cold trap could not be distinguished from the total mixture pressure. Total pressures between .4 and 3.2 torr were investigated for wide variations in water vapor content.

The temperature measured by an ice bulb thermocouple was found to be sensitive to the amount of water vapor in a low vacuum air-water vapor mixture. Satisfactory ice bulb equilibrium could not be achieved with the present equipment, therefore, a successful calibration curve could

not be developed.

A gas analyzer, using a silica gel desiccant, was developed to measure the partial volume of water vapor in a low vacuum mixture. The method involved removing water vapor from a gas sample held at constant pressure and temperature. A lack of sensitivity in this device prevented its application at pressures below 6 torr and resulted in errors up to 10 per cent.

NOMENCLATURE

Symbol	Quantity	Typical Units
A	area	ft^2
C	molal concentration	lbm-moles/ft^3
D_v	mass diffusivity constant	ft^2/hr
k	thermal conductivity	BTU/hr ft F
K	overall mass transfer coefficient	lbm-moles/hr ft^2 atm
m	mass	lbm
$\dot{m}$	mass flowrate	lbm/hr
M	molecular weight	AMU
n	number of moles	lbm-moles
N	molal flowrate	lbm-moles/hr
P	pressure	lbf/ft^2
q	heat flow rate	BTU/hr
R	specific gas constant	ft lbf/lbm R
$\bar{R}$	universal gas constant	ft lbf/lbm-mole R
S	heat of sublimation	BTU/lbm
t	time	hrs.
T	temperature	degrees Fahrenheit
V	volume	ft^3
x	mole fraction	--
Φ	relative humidity	per cent
ω	specific humidity	lbm water/lbm air
τ	a time constant	hr.

Subscripts	Pertains to
1	the large tank
2	the small tank
3	the cold trap
a	constituent a
A	air
b	constituent b
c	constituent c
D	flow by diffusion
i	the ice bulb
M	flow of the mixture
s	a surface
t	time
T	the total mixture
W	water vapor
WS	water vapor at saturation

CHAPTER I

INTRODUCTION

Definition of the Problem

The purpose of this study is to provide a convenient means for determining the amount of water vapor in a mixture of air and water at low vacuum pressures. A laboratory standard provided for this situation will be used as a basis for examining applicable methods.

Mixtures of Ideal Gases

Before considering the nature and significance of humidity measurement at low pressures, it is necessary to become familiar with the terminology used in studying gas and gas-vapor mixtures. Also, it is convenient to use various methods for representing the amount of constituents present in such mixtures and the relationship between these methods should be fully understood. For these reasons, it is appropriate that some of the more important mixture relations be reviewed.

Consider a gas mixture composed of the three constituents a, b, and c. The total mass of this mixture is, of course, the sum of the masses of the constituents,

$$m_T = m_a + m_b + m_c \tag{1}$$

From this equation, it seems quite natural to define the mass fraction of a constituent,

$$\frac{m_a}{m_T} = \text{mass fraction of constituent } a \tag{2}$$

If this same procedure is followed on a molal basis, the total number of moles in a mixture may be represented as

$$n_T = n_a + n_b + n_c \tag{3}$$

A logical definition of the mole fraction may now be written,

$$\frac{n_a}{n_T} = \text{mole fraction of constituent } a = x_a \tag{4}$$

Consider the nature of a gas mixture. Let one gas be observed independently of the others. This gas, while existing at the temperature and volume of the entire mixture, exerts only a portion of the total pressure and it can be shown that, in a mixture of ideal gases, the total pressure is the sum of the partial pressures exerted by all the constituents,

$$P_T = P_a + P_b + P_c \tag{5}$$

This represents Dalton's law of partial pressures.

The somewhat more abstract concept of partial volumes may also be considered. The partial volume of a gas in a mixture is the volume that gas would occupy if it alone were at the pressure and temperature of the mixture. For a mixture of ideal gases, it can be demonstrated that

$$V_T = V_a + V_b + V_c \tag{6}$$

This relation has become known as Amagat's law.

Since each of the concepts presented above -- mass fraction, mole fraction, partial pressure and partial volume -- represent terms which can indicate the amount of a constituent present in a mixture, the terms must now be related.

Let the concept of partial pressure again be considered. The ideal gas equation of state can then be written for the mixture and each of its constituents. Dividing the equation for a constituent by the equation for the mixture results in,

$$\frac{P_a V}{P_T V} = \frac{n_a \bar{R} T}{n_T \bar{R} T} \tag{7}$$

This simplifies to

$$\frac{P_a}{P_T} = \frac{n_a}{n_T} = x_a \tag{8}$$

This same technique can also be applied on the basis of partial volumes,

$$\frac{PV_a}{PV_T} = \frac{n_a \bar{R} T}{n_T \bar{R} T} \tag{9}$$

Simplifying yields,

$$\frac{V_a}{V_T} = \frac{n_a}{n_T} = x_a \tag{10}$$

When an analysis presents the amount of a constituent as a ratio

of its partial volume to the total mixture volume, it is called a volumetric analysis. Equations 8 and 10 show that, for a perfect gas, the volumetric analysis also represents the mole fraction of the constituent and the ratio of its partial pressure to the total mixture pressure. If an analysis uses the mass fractions of constituents to represent their concentrations, it is known as a gravimetric analysis. These two types of analyses may be related in the following manner:

Mole units may be converted to mass units by recalling that

$$m = M n \tag{11}$$

Applying this equation to the constituent and to the total mixture results in,

$$\frac{m_a}{m_T} = \frac{M_a\ n_a}{N_T\ n_T} = \frac{M_a}{M_T}\frac{V_a}{V_T} \tag{12}$$

The equivalent molecular weight of a mixture may be determined by

$$M_T = x_a M_a + x_b M_b + x_c M_c \tag{13}$$

Use of this equation in conjunction with equation 12 provides a convenient means for relating the gravimetric and volumetric analyses.

The constituents of the mixtures considered in this work are restricted to air and water vapor. A standard terminology has developed for this common type of mixture. In this terminology, the terms "specific humidity" and "relative humidity" are frequently used.

The definition of relative humidity is

$$\Phi = \frac{P_w}{P_{ws}} \times 100 \tag{14}$$

where P_{ws} is the pressure of saturated water vapor at the temperature of the mixture under consideration. In the work presented herein, the total pressure is held far below the saturation pressures for the existing temperatures. For this condition, the term relative humidity loses its practical significance and becomes merely an awkward method for indicating the partial pressure of water vapor.

Specific humidity is the ratio of the mass of water vapor to the mass of air present in a mixture, or

$$\omega = \frac{m_w}{m_A} \tag{15}$$

A convenient expression for the specific humidity can be developed by treating the air and water vapor as ideal gases. Recall that for a perfect gas

$$m = \frac{PV}{RT} \tag{16}$$

By combining equations 15 and 16, it can be shown that

$$\omega = \frac{R_A}{R_w} \frac{P_w}{P_A} \tag{17}$$

Inserting the specific gas constants into equation 17 gives

$$\omega = .622 \frac{P_w}{P_A} \tag{18}$$

Specific humidity continues to be a convenient indication of water vapor concentration even at the low total pressures considered here.

Background

Humidity measurement under low vacuum conditions is studied in order to analyze air-water vapor mixtures as they occur in a freeze drying situation. Freeze drying takes place at low vacuum pressures to allow the drying of food products by sublimation.

The importance of knowing the water vapor concentration in such a drying process may be noted from a typical mass transfer equation (4)

$$\frac{N_a}{A} = - \frac{D_v}{\bar{R}T} \frac{dP_a}{dy} \tag{19}$$

This is the equation for one-dimensional molecular diffusion. It is analogous to the equation for one dimensional heat conduction:

$$\frac{q}{A} = -k \frac{dT}{dy} \tag{20}$$

A comparison of equations 19 and 20 shows that knowledge of the partial pressures controlling a drying process is as important as knowing temperatures in the study of heat transfer.

To determine the driving forces in freeze drying and also to determine the necessary material properties, a method of humidity measurement under low vacuum conditions is desired.

Possible Methods

Numerous methods exist for the measurement of humidity under ordinary atmospheric conditions. However, at low pressures and low relative humidities, available methods are not as numerous. The classical methods lose sensitivity and in some cases give no response at all. A

literature search has shown that possible methods do exist for humidity measurement under low vacuum conditions. The most promising of these methods will now be presented, together with an account of the theory involved in their operation.

Electrical Hygrometer

The electrical hygrometer consists of a thin layer of hygroscopic salt deposited upon an electrical insulator. Two electrodes are mounted on the insulator in contact with the hygroscopic film. The resistance of this film is a function of the surrounding temperature and humidity. The hygrometer is calibrated to read relative humidity as a function of resistance at several constant temperatures.

To understand the operation of this element, first consider a salt being dissolved in water. The vapor pressure of this solution is lower than that of pure water. As more salt is added, the vapor pressure continues to decrease until the saturation point is reached. The saturated solution normally presents the lowest vapor pressure that a solution of a particular salt can have at a given temperature.

It has been shown that the vapor pressure exhibited by a solution of water and a hygroscopic salt is inversely related to the amount of salt in solution. It should also be noted that mass transfer occurs between the solution and the surrounding atmosphere to change the solution concentration as required to equalize the solution vapor pressure and the partial pressure of water in the surroundings.

Now consider a thin film of hygroscopic salt as deposited on a hygrometer element. This element is placed in an atmosphere containing water vapor. Water is adsorbed by the salt until it comes into equilibrium

with the surrounding atmosphere. After this initial equilibrium is reached, any change in the humidity of the atmosphere results in an adsorption or release of water by the salt as required to maintain continuous equilibrium with the environment.

The electrical resistance of the hygrometer element depends on the amount of water contained by the salt. According to Schaeffer (5), the specific resistance actually increases at higher humidities. This is due to a change in the ion mobility. However, the increase in volume and cross-sectional area outweighs this increase in specific resistance. An overall decrease in total resistance is the result of high water content surrounding the element.

The electrical hygrometer has certain limitations. The element is limited in its response to low humidities by the solubility of the salt. This is illustrated by considering the mechanism of an exposure to a mixture containing water vapor at a very low partial pressure. The element itself seeks to attain an equally low vapor pressure. However, a saturated salt solution represents the lowest vapor pressure possible at a given temperature. If this pressure at saturation is still above the surrounding partial pressure, the element continues to give off water until it is completely dry. This shows that the lowest humidity which the element can record corresponds to the vapor pressure of the saturated salt solution at the particular temperature being considered.

The high humidity limitation is encountered as 100 per cent relative humidity is approached. This requires the salt solution to move towards infinite dilution. It continually adsorbs water until it begins to "run" and the element is ruined. Special binders can be used to hold

the salt and prevent permanent destruction. However, direct contact with liquid water will still result in damage.

Temperature has two important effects on the element. For a solution of fixed concentration, a change in temperature will result in a change of resistance. In addition, the vapor pressure of this fixed concentration solution depends on temperature.

Consider an element placed in an atmosphere where the partial pressure of water vapor is held constant. Any change in temperature will result in a resistance change by two mechanisms. The resistance of the element will vary because it depends on temperature even if the concentration of solution were held fixed. Also, since the vapor pressure of the solution changes with temperature, a transfer of water to or from the element is necessary. The resulting change in solution concentration causes another change in the hygrometer's resistance.

The effect of total pressure on the hygrometer element has not been specifically mentioned in the literature. It is implied there that pressure variation does not affect its steady state behavior. Morris and Sobel (6) have analyzed the effect of total pressure on the hygrometer's transient response to sudden humidity changes. They found that the transfer of water vapor to and from the hygrometer is primarily controlled by a diffusion mechanism. Since the mass diffusivity constant is an inverse function of the total mixture pressure, transient response is improved at lower pressures. It is suspected that the equilibrium situation is independent of total pressures. According to Sienko and Plane (8) pressures of thousands of atmospheres are required to produce appreciable effects on solid-liquid solutions. This seems to indicate pressure

independence at equilibrium.

In the light of the preceding discussion, electrical hygrometers should be applicable for humidity measurement at low pressures. However, the elements used must be capable of response at relative humidities near one per cent.

Cold Trap

It has been suggested that when a cold trap is placed in a vacuum system containing a mixture of air and water vapor the pressure read at the cold trap is the partial pressure of air in that system.

Consider a liquid nitrogen cold trap inserted into the system described above. The water vapor in the cold trap immediately freezes out. The resulting decrease in concentration causes water vapor to flow towards the cold trap from the remainder of the system. If the volume of the remaining system is large compared to the volume of the cold trap, the mixture in this part of the system will not be affected by the small amount of water flowing into the cold trap and freezing out. A steady state can be reached in which the water vapor flow rate is essentially constant.

Let Figure 1 represent the system under steady state conditions. Water vapor diffuses toward the cold trap ($\dot{m}_{WD}$) due to the concentration gradient. This must be accompanied by a counter diffusion of air out of the cold trap ($\dot{m}_{AD}$). However, the net flow of air must be zero at equilibrium. This requires a flow of the entire mixture into the cold trap. If this flow is hydrodynamic, P_3 is less than P_1 and possibly very close to P_{1A}. However, P_3 may just as easily be close to P_1 and it is even possible that the required bulk flow does not result from a hydrodynamic force. A constant pressure convective flow, similar to that

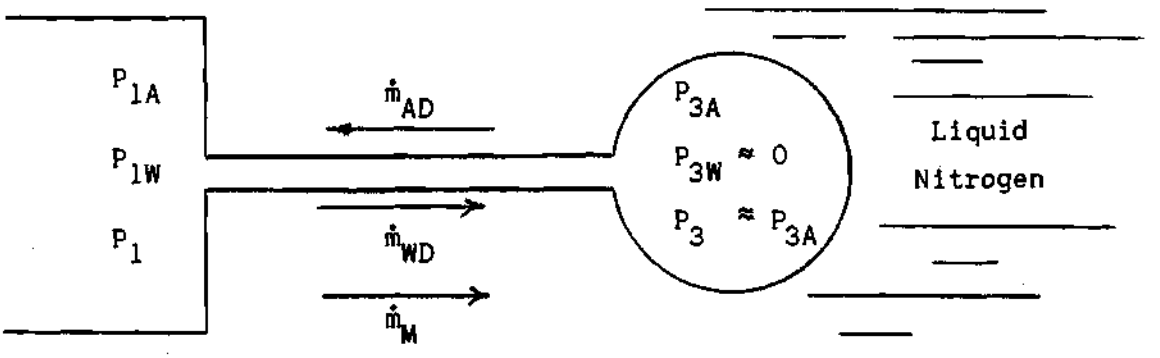

Figure 1. Operation of the Cold Trap.

described in deriving Stefan's Law (3), could cause the bulk movement. The actual situation may depend on the geometry of the system under consideration. It should be noted that this analysis is purely qualitative in nature. Thermal diffusion may be appreciable and should be considered in any complete analysis.

Stallings and Martin (9) have reported measuring cold trap pressures which are equibalent to the partial pressure of air in the remainder of the system. Their data was taken at pressures up to 100 microns in a flowing system.

Dyer's data (10), at a total pressure near 3 torr, show that the cold trap pressure is less than the total pressure but greater than the partial pressure of air. For a constant total pressure, the cold trap pressure showed only slight dependence on the water vapor content of the mixture.

Certain questions arise concerning both of these works. Stallings and Martin measure cold trap pressures in a flowing system. The system is then isolated and several cold traps allowed to remove the water vapor from the system. The resulting pressure is termed the partial pressure

of air in the flowing system and compared with the cold trap reading. However, it is not clear why a pressure, taken at any point in a flowing system, should represent the pressure this system will have when suddenly isolated.

In Dyer's work, it seems possible that the nearly constant difference between the cold trap and total pressures may be inherent in his instrumentation. A calibration check was not made on dry air.

Ice Bulb

The most common means for measuring humidity under atmospheric conditions involves the use of a wet-bulb thermometer. A similar method involving the use of an ice-bulb may be applied under low vacuum conditions.

A thermocouple junction is frozen into a cylinder of ice. The ice is placed in a low vacuum air-water vapor mixture and eventually reaches an equilibrium temperature. This temperature is related to the partial pressure of water vapor in the system.

The relation between temperature and partial pressure should now be considered. At equilibrium, the amount of heat transfer to the subliming ice must be equal to the required heat of sublimation. In equation form,

$$q = SKA_s(P_w - P_i) \qquad (21)$$

The ice temperature has only a relatively small effect on the heat transfer. However, the mass transfer is vastly dependent on this temperature since the ice bulb vapor pressure is a function of temperature alone. This means that for a relatively large variation in surrounding

partial pressures, changes in the amount of heat transfer will be quite small.

Consider now that the ice bulb is in equilibrium and an increase in P_w takes place. Since the heat transfer will not vary appreciably, a change in P_i is required to hold the mass transfer constant. To obtain the increase in P_i, the ice temperature must increase. Therefore, the ice temperature varies directly with the surrounding partial pressure. The relation may be such that a calibration curve can be made. It should be mentioned, however, that the overall mass transfer constant, K, in equation 21 is dependent on total pressure. The considered calibration must thereforebe conducted under constant pressure conditions.

Gas Analysis

The use of a chemical method for extracting water vapor from low humidity mixtures has been demonstrated by Thuman and Robinson (11). They used absolute methanol as an extractor in the investigation of humidities at temperatures ranging from -4 F to -67 F. Their exact method is not applicable for the conditions encountered here, but it does indicate that small amounts of water vapor can be removed from a mixture by chemical means.

A gas analyzer, similar to the Orsat analyzer used in the study of combustion, may be applicable for measuring humidities at low vacuum conditions. This method would involve taking a sample of the desired mixture and exposing it to a desiccant. This will remove the water vapor from the sample. If the gas is held at a constant temperature and pressure, the change in volume will indicate the partial volume of water vapor in the original sample.

Dew Point

A certain surface is exposed to a mixture of air and water vapor. Lowering the temperature of this surface corresponds to constant pressure cooling of the surrounding mixture. When condensate appears on the cooled surface, the temperature of the surface is at the mixture's dew point temperature.

In practical use of this method, the temperature must be recorded at the first hint of dew or frost deposit. Two difficulties arise: the temperature is transient when the first deposit forms, and the accuracy is limited by the ability of an observer to detect this first deposit.

Special equipment has been developed to overcome these difficulties. Phototubes have been used (13 and 14) to detect the initial deposit and then control the cooling system to maintain the dew point temperature. Clack (15) determined the dew point within a discharge tube by noting a variation in the voltage drop across the glow discharge as the tube was cooled. In a recent development (16), a thermoelectric device was used to replace the combined heater and refrigerant formerly needed for controlled cooling. This should allow more convenient use of the dew point method. Former heater and refrigerant combinations usually involved dry ice and alcohol baths combined with an induction heater.

The use of a dew point method offers considerable possibilities. However, to achieve appreciable accuracies, somewhat complex equipment must be applied.

Purpose of the Study

The methods presented above were considered for application at low vacuum pressures. Primarily because of the equipment difficulties which

could be anticipated for low vacuum operation, the dew point method was not investigated.

Measurement of humidity under low vacuum conditions will be investigated by a commercial electrical hygrometer, a liquid nitrogen cold trap, an ice-bulb thermocouple, and a gas analyzer. A previously developed laboratory standard (17) will be used as a basis for this investigation.

CHAPTER II

INSTRUMENTATION AND EQUIPMENT

The Pressure Instrumentation

Various equipment arrangements were used in the course of the experimental investigation. However, essentially the same instruments were used for pressure measurement during each of the tests. These instruments will be discussed here and their use in specific tests will be explained as each equipment arrangement is presented.

A convenient means of measuring low pressures was necessary for assembling and checking out the vacuum system. An NRC thermocouple gage was employed to monitor pressures from 5 to 1000 microns. This gage was not very accurate and its operation was affected by the presence of foreign gases and vapors. However, it served as an excellent tool for leak detection and was used to maintain a continuous measurement of the system pressure.

A micromanometer, manufactured by the Roger Gilmont Instrument Corporation, was an important part of the pressure instrumentation. The micromanometer was vacuum sealed and its micrometer dial could be read to one-thousandth of an inch. Contact of the micrometer needle with the fluid surface was observed by noticing the scatter of surface reflections when the needle touched the meniscus. Readings taken in this manner were easily reproduced.

The fluid used in the micromanometer was a Dow Corning Silicone

product with a low vapor pressure. Its specific gravity was determined with a hydrometer and also by measuring the weight of a known fluid volume. Both methods indicated a fluid specific gravity of .916.

The micromanometer, with the silicone fluid, was readily applied to the measurement of differential pressures under vacuum conditions. It was also adapted to measure absolute pressures. A reference pressure was provided on the low pressure side of the manometer by keeping it open to the vacuum pump. This pressure was measured by the NRC thermocouple gage and it was held in the range of 5 to 10 microns. The reference pressure was very small as compared to pressures considered on the other side of the fluid. Therefore, the manometer read essentially absolute pressure. A correction for the reference pressure was added for improved accuracy. This correction was always less than 2 per cent of the absolute pressure so the accuracy of the thermocouple gage was not critical. Pressure measurements of considerable accuracy could be made at pressures above .4 torr. These measurements were independent of the water vapor content of the vacuum system.

A McCleod type vacuum gage was used to obtain accurate measurements of pressures below 1 torr. This gage was also made by the Roger Gilmont Instrument Corporation. As with all gages operating on the McCleod principle, it could only be used on dry air.

The final pressure instrument to be discussed is a Wallace and Tiernan vacuum gage. This gage measures an unknown pressure by using a mechanical linkage to determine its effect on a sensitive metal capsule. The linkage actuates a pointer which moves across a scale covering the pressure range from .1 to 20 torr. Because of its mechanical nature, it functions independently of the water vapor content of the vacuum system.

Humidity Measurement and Control

A method presented by Dyer and Sunderland (17) was used as a basis for determining the humidity inside the vacuum system. This method involved measuring the water vapor content of the vacuum mixture by using an auxillary tank in conjunction with the main vacuum system. A mixture of uniform moisture content was established throughout the system and its pressure and temperature were measured. A valve was closed to isolate the second tank. This tank was then submerged in liquid nitrogen and the water vapor was frozen out of the mixture. The remaining pressure was due only to air at the temperature of liquid nitrogen. By means of the ideal gas equation of state, the partial pressure of air in the original system was determined. An analysis of the initial air-water vapor mixture could then be made as discussed in Chapter I.

It seemed possible to establish a mixture of known content by controlling the amounts of air and water vapor in the vacuum system. The proposed method of control began by admitting atmospheric air into a well evacuated system and pumping it down to a certain desired pressure. This pressure was recorded. Water was then allowed to flow into the vacuum system by briefly opening a pinch clamp placed on a length of plastic tubing whose open end was filled with distilled water. The water admitted quickly vaporized and filled the system. The pressure indicated after complete evaporation was the total pressure of the air-water vapor mixture. Atmospheric air normally contains less than two per cent water vapor by volume. Therefore, the water present in the initial sample of air could be neglected when compared to the relatively large amount of distilled water admitted through the pinch clamp. Any

air dissolved in the admitted water could be neglected because of the large increase in specific volume when water changes phase. The partial pressure of air in the final mixture was considered to be the system pressure prior to the addition of water vapor. The mixture analysis could then be determined.

After a mixture of known composition was established in the vacuum system, new total pressures were obtained by slightly opening the valve to the vacuum pump. The Welch Duo-Seal vacuum pump operated at a relatively low speed of 300 RPM. This permitted the pump chambers to completely fill during each revolution and thus remove small "chunks" from the vacuum system with the same content as the established mixture. Specific humidity then remained constant while reaching lower pressures.

The laboratory standard proposed by Dyer was used to check this method of humidity control before accepting its reliability. A further check was made while investigating the electrical humidity sensors.

Investigation of the Electrical Transducers

Narrow range humidity transducers manufactured by Hygrodynamics Incorporated* were selected for investigation at low vacuum pressures. The basic design of these transducers is described by Dunmore (18). Particular merits of these elements include high sensitivity at low humidities, rapid response to sudden humidity changes and the absence of hysteresis effects. Three separate transducers were used to provide optimum sensitivity for the range from 1 to 15 per cent relative humidity.

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*Hygrodynamics Incorporated, 949 Selin Road, Silver Spring, Maryland.

The resistance of the sensing elements was not measured directly. Read out equipment manufactured by Hygrodynamics was used. This equipment allowed current readings to be made which were related to the transducer resistance. The read out equipment passed an alternating current through the element to avoid polarizing it. This alternating current was then converted to a direct current. The direct current was measured on a microammeter with a full scale reading of 100 microamps. It was also possible to pass this current through known resistors and use the voltage drop as input to an ordinary strip chart recorder. The ammeter alone served sufficiently well for this investigation.

Calibration curves were supplied with the sensing elements. In these curves, relative humidity was plotted against current readings from the output equipment. Since this calibration is temperature dependent, the plots were made along isothermal lines. It was desired to investigate the validity of these curves at low vacuum conditions.

The equipment shown in Figure 2 was used in evaluating the electrical transducers and also to check the proposed method for controlling humidity. The pressure instrumentation was arranged so that the Wallace and Tiernan gage could constantly monitor the system pressure. The RGI manometer (no. 1) was used to take precise measurements of the absolute pressure and also to check the Wallace and Tiernan calibration. The McCleod gage was used to measure the pressure of tank 2 after it was submerged in liquid nitrogen. Another RGI manometer (no. 2) was used to aid in establishing equivalent mixtures in the two tanks. It was found (see Appendix A) that if the tanks did not initially contain the same mixture, a considerable amount of time was required for the mixtures to

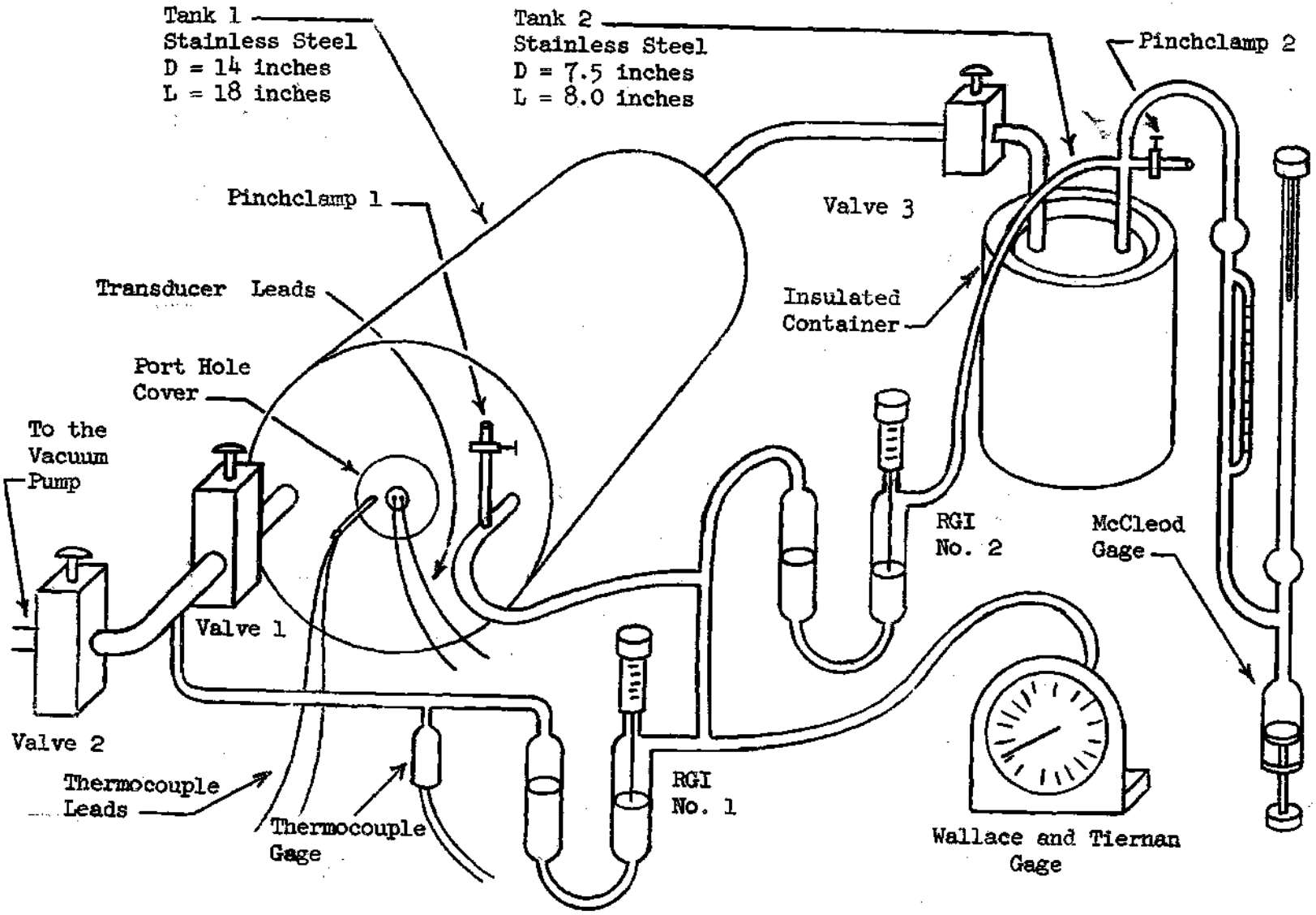


Figure 2. Transducer Calibration Using the Laboratory Standard

combine and reach an equilibrium concentration. The method used to obtain a consistent mixture is outlined in the Experimental Procedure. A measure of differential pressure was required and the RGI manometer provided it.

The temperature of tank 1 had to be determined for use with the laboratory standard and also because of the temperature dependence of the transducer. A copper constantan thermocouple, calibrated against a thermometer certified by the National Bureau of Standards, was used to measure this temperature. The thermocouple and transducer were placed in the vacuum system through feed throughs in the port hole cover shown in Figure 2. The port hole was 2.25 inches in diameter and its cover was vacuum sealed with a teflon O-ring.

After showing that the proposed method of humidity control performed satisfactorily, the laboratory standard was omitted from the calibration equipment. Valve number 3, between the two tanks, was closed and tank 1 was used alone to obtain the remaining calibration data.

The Cold Trap Investigation

The operation of a cold trap was discussed in Chapter I. It was desired to determine the relation between the total pressure of a low vacuum air-water vapor mixture and the pressure measured at a cold trap placed in the vacuum system. The experimental equipment is shown in Figure 3. Measurements of the total pressure and the cold trap pressure could be made with various amounts of water vapor in the vacuum system. The tank used was large enough to reach the steady state conditions discussed in Chapter I.

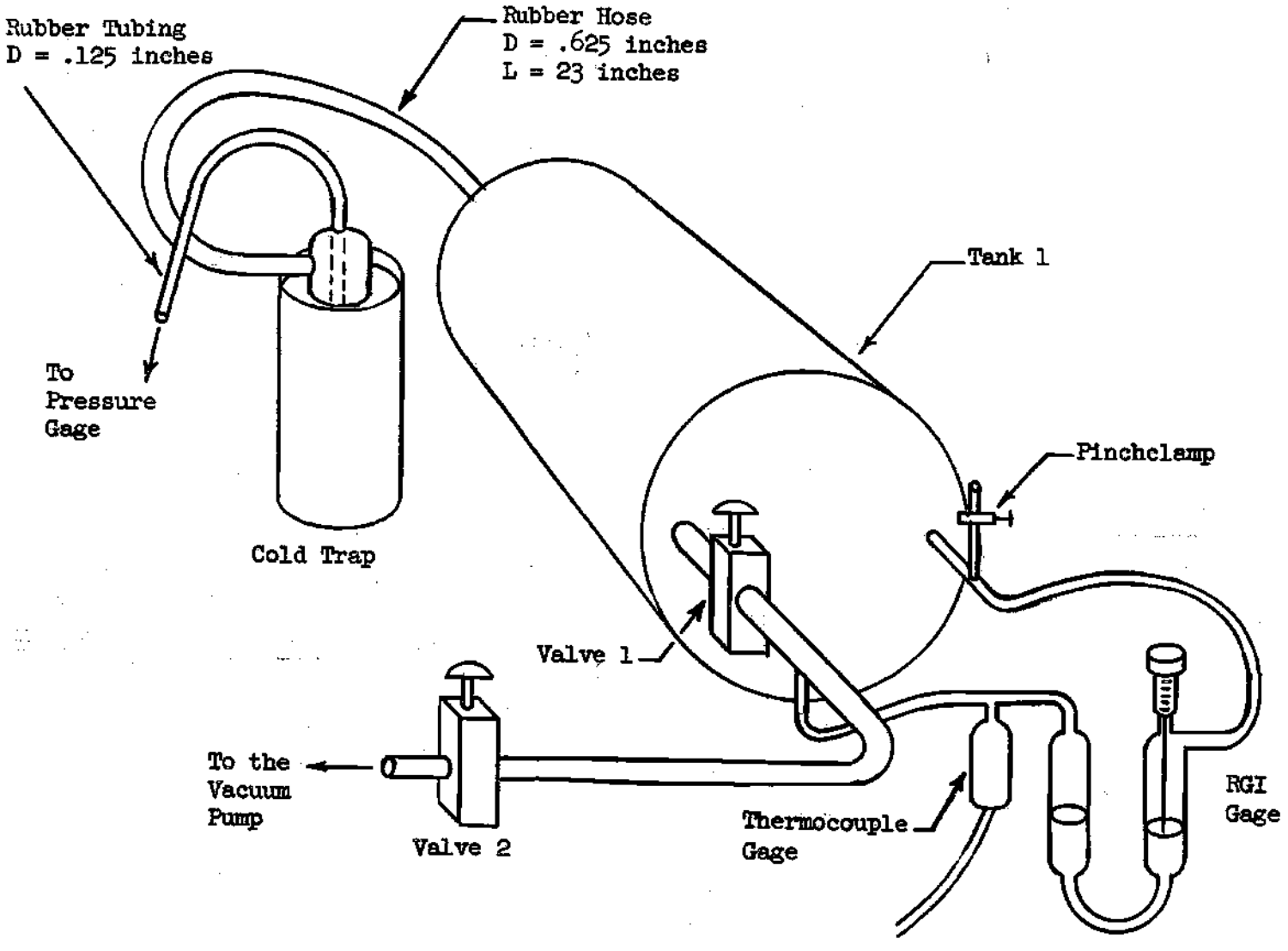


Figure 3. Apparatus for the Cold Trap Investigation

The total pressure of the system was measured by the RGI micromanometer as set up for the measurement of absolute pressures. Two gages were needed to measure the cold trap pressure. The Wallace and Tiernan gage was used for pressures between 1 and 3 torr. At pressures below 1 torr, the McCleod gage provided better accuracy. A comparison of the pressure gages was made on dry air. The McCleod gage and micromanometer were in excellent agreement. The Wallace and Tiernan gage was calibrated to read correctly.

The mixture of air and water vapor within the vacuum system was controlled by admitting air and water through the pinchclamp shown in Figure 3. The initial mixture analysis was determined by measuring the pressure after the air and the water had each been admitted. Constant specific humidity was assumed as the system was pumped to lower pressures.

The equipment in Figure 3 was used to investigate the relation between the cold trap and total pressures at various specific humidities. Pressures ranging from .4 to 3 torr were considered.

The Ice Bulb Thermocouple

The possibility of using an ice bulb thermocouple to measure humidity at low vacuum conditions was introduced in Chapter I. A calibration of the ice bulb temperature versus the partial pressure of water vapor was attempted for a constant pressure of 3 torr. The following equipment was used in this calibration.

A thermocouple, which had been checked against a National Bureau of Standards thermometer, was frozen in the center of an ice cylinder. The arrangement is shown in Figure 4.

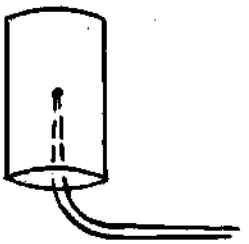


Figure 4. The Ice Bulb Thermocouple.

The cylinder was formed from distilled water and diameters of 3/8 and 3/4 of an inch were considered. The thermocouple leads were placed along the axis of the ice cylinder to minimize the effect of heat conduction along the wires to the thermocouple junction.

The ice bulb was suspended in the vacuum system from the end of a one foot rod which was fastened to the port hole cover. The cylinder was supported by the thermocouple leads. Valve number 3 was closed and only tank 1 was used.

The water vapor content of the vacuum chamber was obtained from an electrical transducer placed in the system. The transducer used (element 4-4815) covered the range from 6-15 per cent relative humidity.

The total pressure was the only pressure measurement required. It was obtained by using the RGI manometer and the Wallace and Tiernan gage. These gages were set up as shown in Figure 2 for investigation of the electrical hygrometers.

The Gas Analyzing Equipment

The equipment used for the gas analysis is shown in Figure 5. It was connected to the rear of tank 1 at the same point where the cold trap and tank 2 had each been placed.

This gas analysis equipment operated in a manner similar to an Orsat analyzer. However, the usual Orsat system uses various liquids to extract selected gases from a mixture under analysis. Silica gel, a solid desiccant was used in this equipment and required special considerations.

The difficulty with the solid desiccant was overcome by trapping dry air in the desiccant container at the same pressure as the rest of the vacuum system. This dry air was obtained by opening pinch clamp 5 with pinch clamp 3 closed and the fluid level at the 100 ml. mark on the gas burette. Mixture was admitted and dried by the desiccant. When pinch clamp 5 could be closed and the levels of the fluid in the levelling bottle and in the burette aligned at the 100 ml. mark, the desired amount of dry air was present. Admitting this amount of mixture to the desiccant container did not cause an appreciable change in the remaining system.

A sample of the vacuum mixture could then be taken. Pinch clamp 4 was closed and the fluid level then brought down to the zero mark on the burette. Pinch clamp 3 was opened and when the fluid levels could be aligned at the zero mark, it was closed. A sample of 100 ml. was thus obtained from the vacuum system.

The sample was dried by raising the leveling bulb to place the entire mixture in the desiccant container. The sample was held in the container for several minutes to allow complete drying. Finally, the leveling bulb was lowered until the fluid surfaces in it and the gas burette were again aligned. The burette reading at this point indicated the partial volume of the water vapor in the original 100 ml. sample. This is sufficient information to define the mixture analysis.

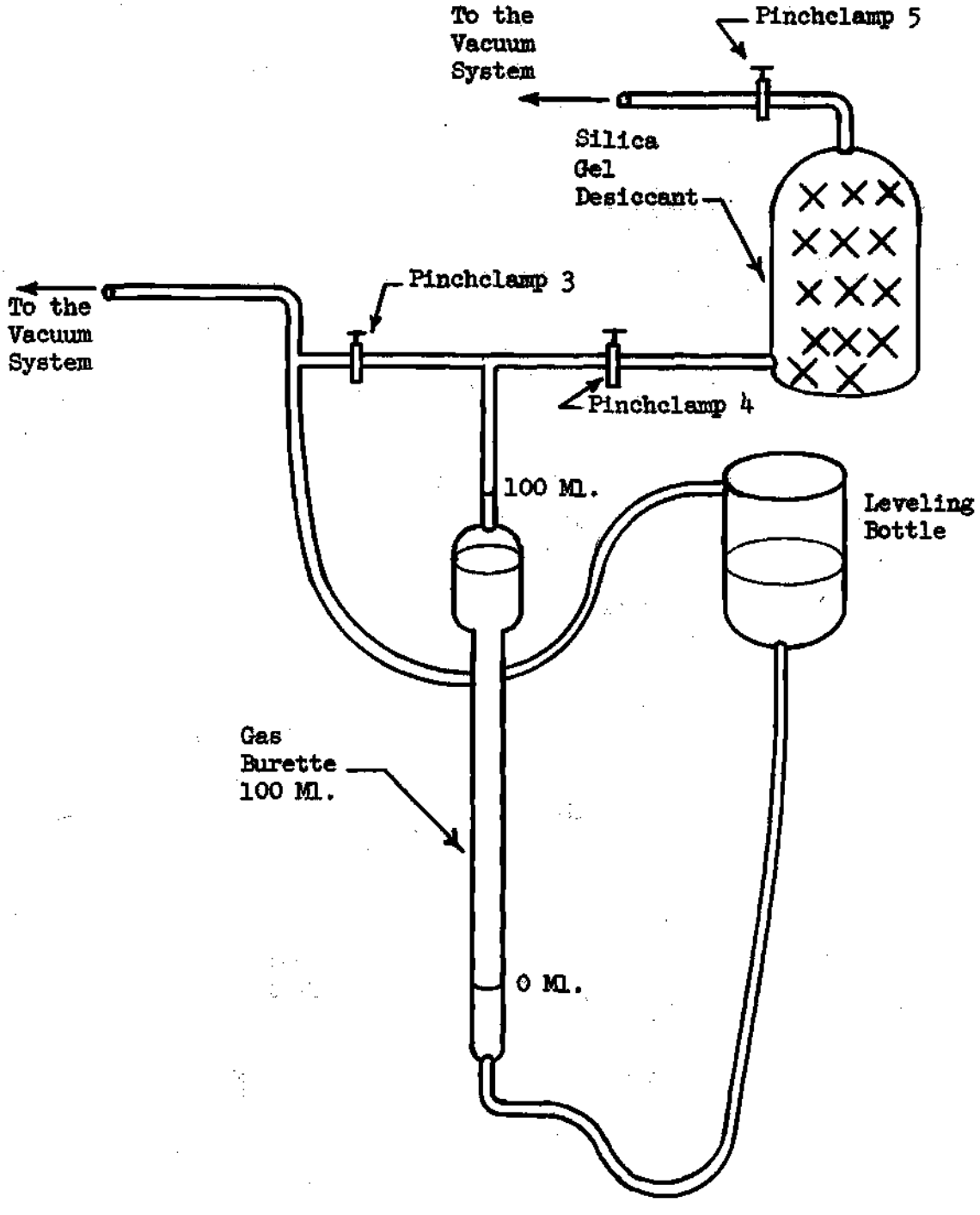


Figure 5. The Gas Analysis Equipment

The mixture was originally set up in tank 1 and its analysis determined by admitting air and water as described in the transducer investigation. The required pressure measurements were made by the Wallace and Tiernan gage and the RGI micromanometer as set up for measuring absolute pressure.

CHAPTER III

EXPERIMENTAL PROCEDURE

The Transducer Investigation

The procedure followed in investigating the electrical transducers could be divided into two parts. In one part, the proposed method for humidity control was investigated along with the transducer. After this method of humidity control was shown to be valid, it alone was applied to checking the electrical transducers. Both procedures will be presented here. The equipment was arranged as shown in Figure 2.

Checking ~~the~~ Method of Humidity Control

During this part of the investigation, data was taken to calibrate an electrical transducer and to verify the method of humidity control. The following procedure was used:

1. The read out equipment for the thermocouple gage and the humidity transducer was turned on and allowed to warm up.

2. A temporary cover was placed over the port hole in tank 1.

3. To remove any contaminating vapors or gases from the vacuum system, valves 1, 2 and 3 were opened and tanks 1 and 2 were evacuated until a pressure of 5 to 10 microns was indicated by the thermocouple gage.

4. Valve 1 was closed and the temporary port hole cover removed. The regular cover, containing the humidity transducer and the thermocouple junction, was promptly placed in position. Valve 1 was again opened.

5. The system pressure was measured with the Wallace and Tiernan gage. Valve 2 was closed when the desired pressure was reached.

6. The reading of both micromanometers was recorded. Since valves 1 and 3 were open, this corresponded to zero pressure differential.

7. Valve 1 was closed and valve 2 opened.

8. When the thermocouple gage showed a pressure of 5 to 10 microns, a reading was taken on manometer 1. Since the gas in both tanks was essentially dry air, this reading indicated the partial pressure of air in the final mixture.

9. The manometer reading was checked several times to make certain that leaks or transients did not cause a change of pressure within the system.

10. Valve 3 was closed to allow equivalent mixtures to be established in tanks 1 and 2.

11. Pinchclamp 1 was briefly opened to allow distilled water to enter tank 1. The pressure then increased until the water was completely evaporated.

12. Pinchclamp 2 was opened to admit distilled water into tank 2. Only enough was admitted to return manometer 2 to its zero position. Tanks 1 and 2 then contained mixtures of equal concentration.

13. Valve 3 was opened.

14. Readings of the temperature, transducer output and total pressure were then recorded.

15. The pressure was lowered by opening valve 1 to bleed out a portion of the mixture.

16. Time was allowed for the system to return to equilibrium and for the manometer reference pressure to reach 5 to 10 microns. New transducer and pressure readings were taken.

17. Steps 15 and 16 were repeated until the lowest desired total pressure was reached.

18. Valve 3 was closed.

19. Liquid nitrogen was added to the container surrounding tank 2 until the tank was totally submerged.

20. The pressure of tank 2 was measured with the McCleod gage.

The liquid nitrogen was drained from the jacket surrounding tank 2 after the McCleod gage reading was recorded. The humidity transducer was removed from the system and the temporary port hole cover was put back in place. Valves 1, 2 and 3 were opened and the pump applied to the system to prevent any contamination during shut down. Several hours were allowed for the system to return to ambient temperature before another run was made.

Applying the Method of Humidity Control

After the method of humidity control was verified, it was used directly in the transducer investigation. Use of the control followed essentially the first nine steps of the procedure just presented. However, since tank 2 was not needed, valve 3 was closed at the start of each run and remained closed throughout. The remaining steps are as follows:

10. A very small amount of water was admitted through pinch clamp 1.

11. When the water had completely evaporated, the new pressure, the transducer output and the temperature was recorded. The partial

pressure of water vapor at that instant was the change in pressure from that recorded in step 8.

12. Steps 10 and 11 were repeated until the desired amount of water vapor was present in the mixture.

13. After making certain that the evaporation of water had stopped, more data was obtained by bleeding out a portion of the mixture through valve 1. This lowered the system pressure.

14. Pressure and transducer output were recorded. The water vapor content was known since the specific humidity remained constant.

15. Steps 13 and 14 were repeated until the lowest desired transducer output was recorded.

After the final data was recorded, the transducer was removed from the system and the temporary cover placed over the port hole. Valve 1 was opened and the pump was allowed to remove all of the vapor and air before beginning another run.

The Cold Trap Investigation

The equipment shown in Figure 3 was used in the investigation of cold trap pressures. The procedure follows:

1. Valves 1 and 2 were opened and the pump was used to bring the system down to a pressure of 5 to 10 microns as indicated by the thermocouple gage.

2. Valve 2 was closed and the system allowed to stabilize. The thermocouple gage was observed to make certain that any pressure rise was negligible compared to the pressures under consideration.

3. The flask of liquid nitrogen was brought up under the cold trap.

4. The line to the pump was opened to the atmosphere and valve 2 was briefly opened to allow a small amount of air to be brought into the system. The valve was securely closed.

5. A zero reading was taken on the manometer.

6. Valve 1 was closed and valve 2 opened to the vacuum pump.

7. When the thermocouple gage read 5 to 10 millitorr a pressure reading could be taken with the micromanometer. Valve 1 could be briefly opened to lower the system pressure to that desired.

8. The micromanometer pressure was compared to the cold trap pressure to insure their equality.

9. Water was added by opening the pinchclamp and allowing a small amount of distilled water to enter the system.

10. After waiting a considerable time for complete evaporation of the water new pressure readings were taken.

11. Lower pressures were obtained by opening and closing valve 1 to exhaust a portion of the mixture.

12. When equilibrium and a low reference pressure were attained, the cold trap and total pressures were recorded.

Steps 11 and 12 were repeated until the lowest desired pressure was reached. Valves 1 and 2 were then opened to the pump and the system was readied for another run.

The Ice Bulb Thermocouple

In attempting to calibrate the ice bulb shown in Figure 4, the equipment was arranged as in Figure 2 and valve 3 was closed. The following procedure was then used:

1. The ice bulb thermocouple, humidity transducer and the ordinary thermocouple were inserted into tank 1.

2. Valves 1 and 2 were opened to the vacuum pump.

3. Valve 1 was closed when the system pressure reached 3 torr. This pressure was measured by the Wallace and Tiernan gage after calibrating it against the RGI manometer.

4. The temperature of the system was recorded.

5. Valve 1 was adjusted to hold the pressure at 3 torr while the ice bulb sublimed.

6. As the humidity slowly increased, the ice bulb temperature and the transducer output were recorded at several points.

7. When desired, the humidity was decreased by admitting air through the pinch clamp.

8. Valve 1 was then regulated to return the pressure to 3 torr and hold it there. Step 6 was repeated.

The calibration curve was expected to cover a fairly wide range of water vapor concentrations. To cover such a range as completely as possible, steps 6, 7 and 8 were repeated a number of times. The desired amount of data could thus be obtained for each ice bulb specimen.

After the data had been recorded, the transducer and the ice bulb were removed from the system. The temporary port hole cover was put in place and the vacuum system was opened to the pump until ready for another run.

The Gas Analysis

The apparatus shown in Figure 5 was connected to the rear of tank 1. It could then be used to analyze air water vapor mixtures placed in

the tank. It should be remembered that "matching the fluid levels" requires equal pressures on both sides of the leveling fluid. The following procedure was used in investigating this equipment:

1. The porthole cover was placed in position to seal tank 1. Valves 1 and 2 (as in Figure 2) and the pinchclamps on the gas analyzer were opened.

2. The vacuum pump was allowed to bring the entire system down to a pressure of 5 to 10 microns.

3. Valve 1 was closed.

4. Pinchclamp 5 (Figure 5) was closed and an additional clamp was placed on the line joining the vacuum system to the burette side of the desiccant container. This clamp was positioned as close as possible to the vacuum system and was tightly closed.

5. The line to the vacuum pump was opened to the atmosphere and valve 1 was opened very briefly to admit air to the system.

6. The pressure was recorded.

7. Water was then added to bring the pressure up to about 6 torr. A brief wait was allowed to be certain evaporation was complete. The exact pressure was recorded.

8. Pinchclamp 3 on the gas analyzer was closed.

9. The clamp was removed from the line to the burette side of the desiccant container.

10. Pinchclamp 5 was opened until the fluid levels could be matched at the 100 ml. mark on the gas burette. Pinchclamp 5 was securely closed.

11. Pinchclamp 4 was closed.

12. The leveling bulb was lowered to a position near the zero mark on the gas burette.

13. Pinchclamp 3 was opened until the fluid levels matched at the zero mark. Pinchclamp 3 was closed.

14. Pinchclamp 4 was opened.

15. The leveling bulb was raised to force the entire mixture into the desiccant container. The mixture was held there for a few minutes.

16. The fluid levels were then matched up and the burette reading recorded.

To be certain that the desiccant had completed its removal of water from the mixture, steps 15 and 16 were repeated. After a few repetitions, the final burette reading was assumed valid.

The entire system was opened to the vacuum pump until another run began.

CHAPTER IV

DISCUSSION OF RESULTS

A Check on the Method of Humidity Control

Figure 6 shows the results of the preliminary check on the method proposed to control the air-water vapor mixture in the vacuum system. The specific humidity after a portion of the original mixture was pumped from the system is shown plotted against the initial specific humidity. The final mixture was analyzed with the laboratory standard. The initial content was controlled by the amounts of air and water placed in the system.

A 45 degree line has been drawn on the axes of Figure 6. Observation of the plotted points in relation to this line shows that the assumption of constant specific humidity was valid for the evacuation of a constant volume tank with the Welch Duo-Seal vacuum pump.

The data were obtained over a range of initial pressures between 3.25 and 7.00 torr. The final pressures considered were between .55 and 2.00 torr. When applying this humidity control, care was taken to avoid appreciable deviation from the pressure and humidity ranges investigated here.

Further evidence that the humidity control functioned as expected was noted throughout the experimental investigation. This evidence will be presented as appropriate in discussing the remaining results.

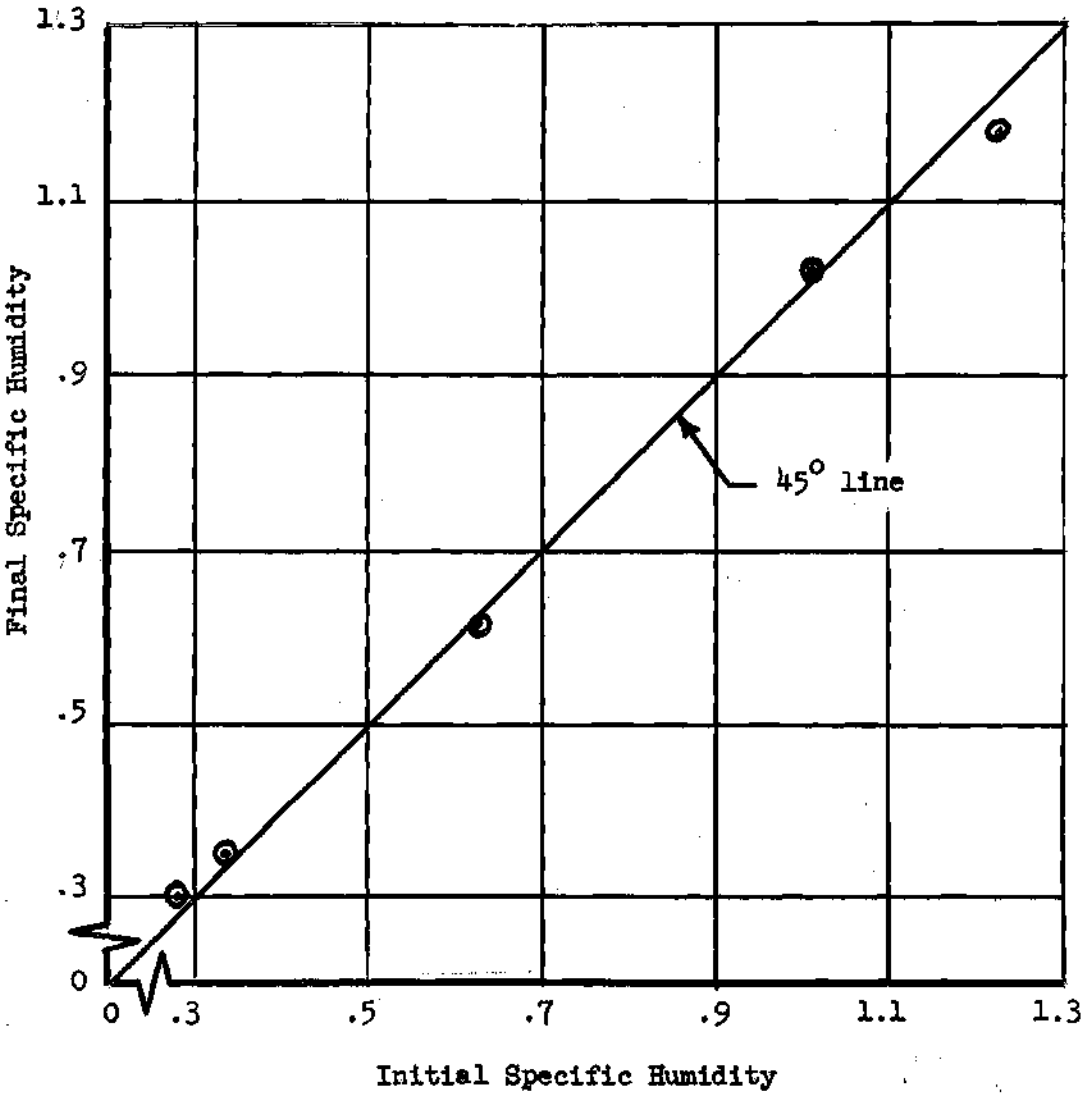


Figure 6. Final Specific Humidity versus Initial Specific Humidity

The Electrical Transducers

The calibration curve generated for the lowest range humidity transducer is shown in Figure 7. This curve was developed while checking the humidity control. The points shown on the graph were determined at various total pressures for a number of constant specific humidities ranging from about .3 to 1.2 lbs. of water per lb. of air.

The curve was plotted for a constant temperature of 80F. Data taken at slightly different temperatures were corrected to 80F with the calibration curve supplied by the manufacturer. It should be noted that the generated curve agrees nicely with points taken from the commercial calibration. Noticeable deviations are restricted to the extremes of the transducer range. Since a variety of total pressures were encountered in generating this curve, the transducer evidently functions independent of total pressure.

Slightly higher range humidity sensing elements were used in developing the curves presented in Figures 8 and 9. These curves were also plotted for a constant temperature of 80F. Satisfactory agreement with the commercial calibration was again experienced.

The procedure used to obtain data for these transducers has been previously described. This procedure offered an opportunity to again check the method of humidity control. Readings of the transducer output were taken as water vapor was admitted to the system and also as the system was pumped to lower pressures. The data obtained for both cases is shown in Figures 8 and 9. Differences could not be detected in the results yielded by the two different methods. This verifies the method of humidity control and the assumptions made as it was proposed in Chapter II.

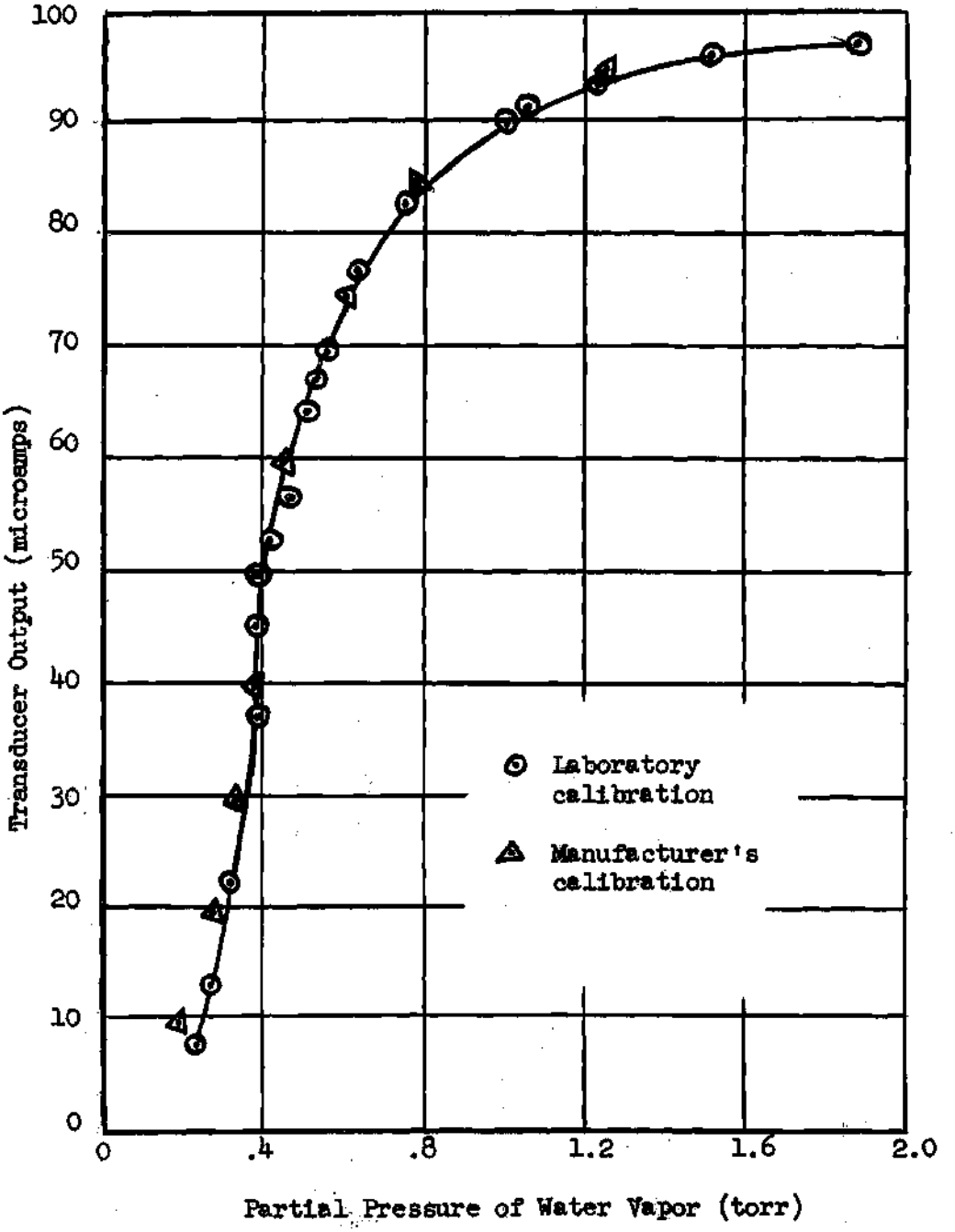


Figure 7. The Relation of Transducer Output to the Partial Pressure of Water Vapor (Element 4-4812, T = 80 F)

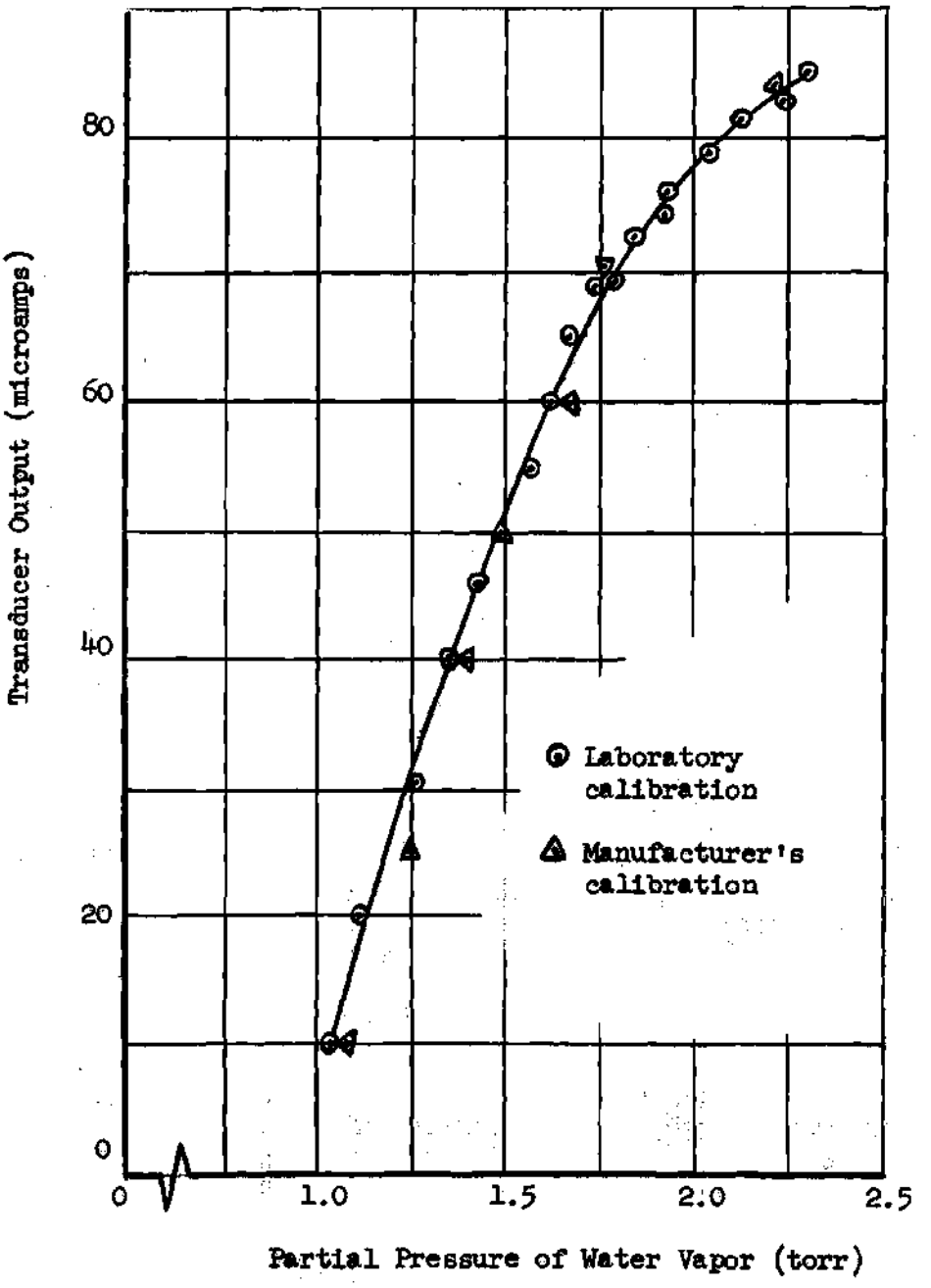


Figure 8. The Relation of Transducer Output to the Partial Pressure of Water Vapor (Element 4-4814, T = 80 F)

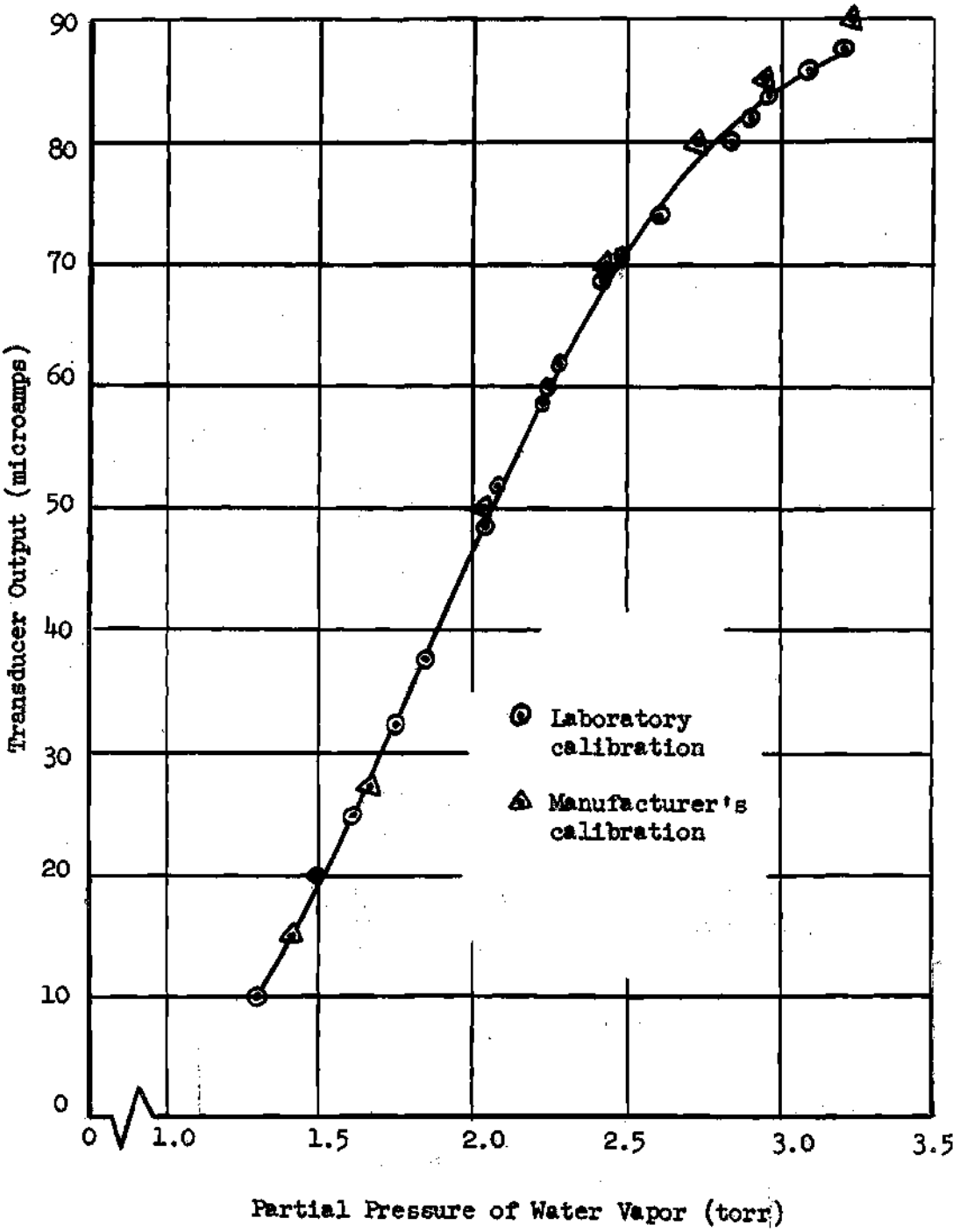


Figure 9. The Relation of Transducer Output to the Partial Pressure of Water Vapor (Element 4-4815, T = 80 F)

It was not convenient to cover a wide range of temperatures in investigating the operation of these commercial transducers. However, temperatures between 75 F and 85 F were considered and satisfactory results were obtained. After a transducer had been used to investigate the freeze drying of beef over a 48 hour period, a calibration check was made at each of the above temperatures. Again, no appreciable deviations were noticed.

It should be mentioned that a calibration shift was experienced for the low range transducer. This shift is discussed in Appendix B and resulted from contamination during the laboratory work.

The Cold Trap Investigation

The results of this investigation are illustrated in Figure 10. On this graph, cold trap pressure is plotted as a function of the total mixture pressure for various specific humidities. The line shown on the graph was drawn at 45 degrees to the axes. The plotted points show, for the range of pressures considered, that the cold trap and total mixture pressures cannot be distinguished from each other. If the bulk flow required by the mass transfer analysis is hydrodynamic in nature, the pressure drop causing it is too small to be detected by the current instrumentation. A constant pressure situation seems to exist for the humidity and pressure ranges investigated.

An effort was made to determine the effect of changing the cross-sectional area of the cold trap connecting hose. A clamp was placed on the connecting hose to restrict flow to the cold trap. As may have been expected from flow considerations, the situation did not change and the

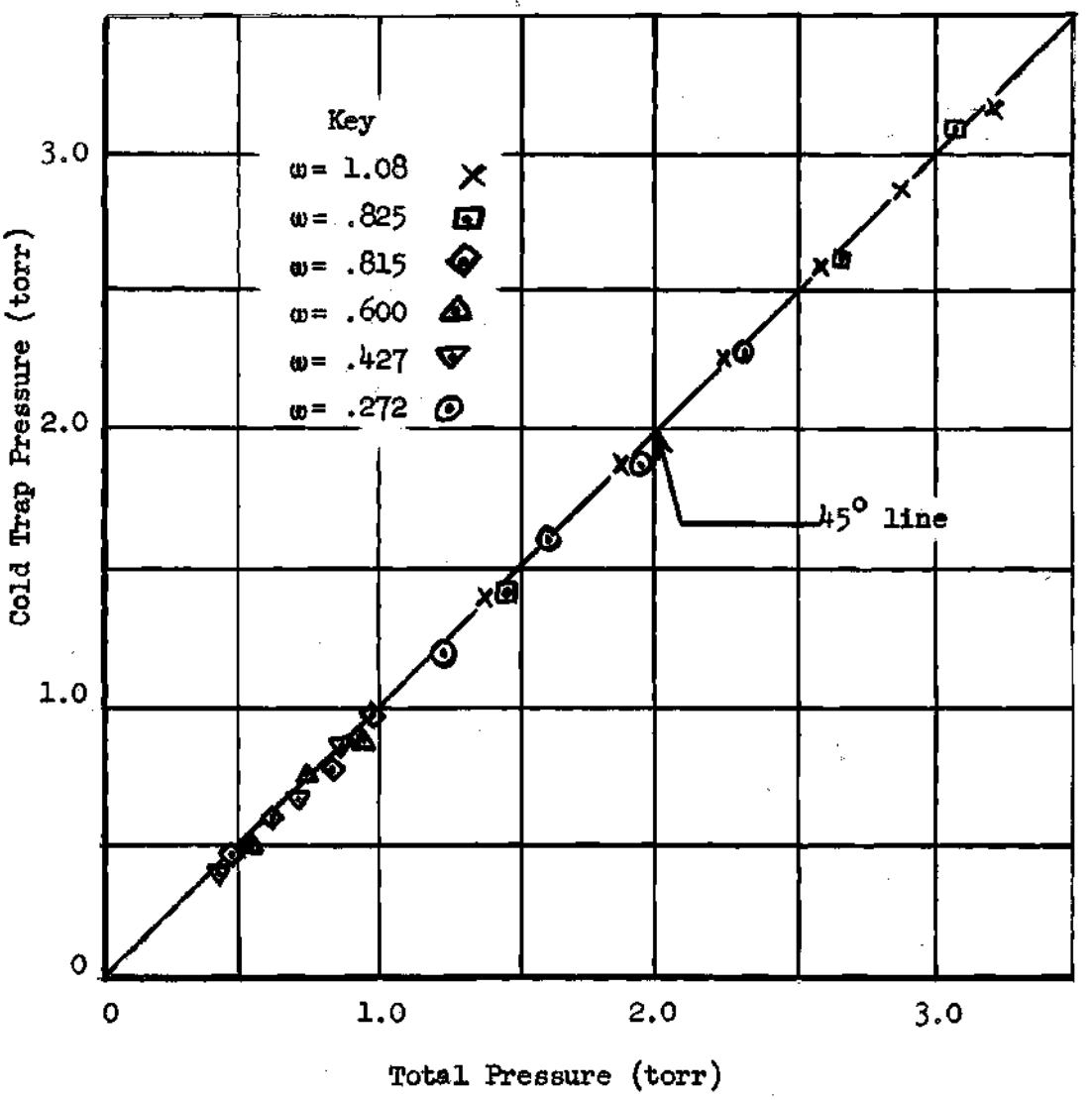


Figure 10. The Relation of Cold Trap Pressure to Total Pressure

measured pressures remained essentially equal.

Using the cold trap to remove the water vapor from the vacuum system offered another opportunity to check the validity of the humidity control. Since the volume of the system was made large to allow quasi-steady state measurements, a long time was required to remove all the water vapor from the system. However, the control check was made by simply closing valve 1 (in Figure 3) after the lowest desired pressure had been reached. The cold trap thus pumped all the water vapor from the system after a period of several hours. The equilibrium pressure differed slightly from the expected partial pressure of air. The measured leak rate corrected this difference. The method for humidity control was again verified.

The Ice Bulb Thermocouple

Attempts to calibrate an ice bulb thermocouple were not successful. Individual ice bulbs showed the expected increase in temperature with increased humidity. However, the data showed considerable scatter and could not be repeated for different ice bulbs. Figures 11 and 12 show the results of the calibration attempts for the two ice bulb sizes considered.

Two explanations for the calibration difficulty are possible. Conduction along the thermocouple leads may effect the measured temperature and the magnitude of this effect may be different for each specimen. It is also possible that the entire ice sample does not reach a uniform temperature. This means that the position of the thermocouple junction in the cross section may be critical.

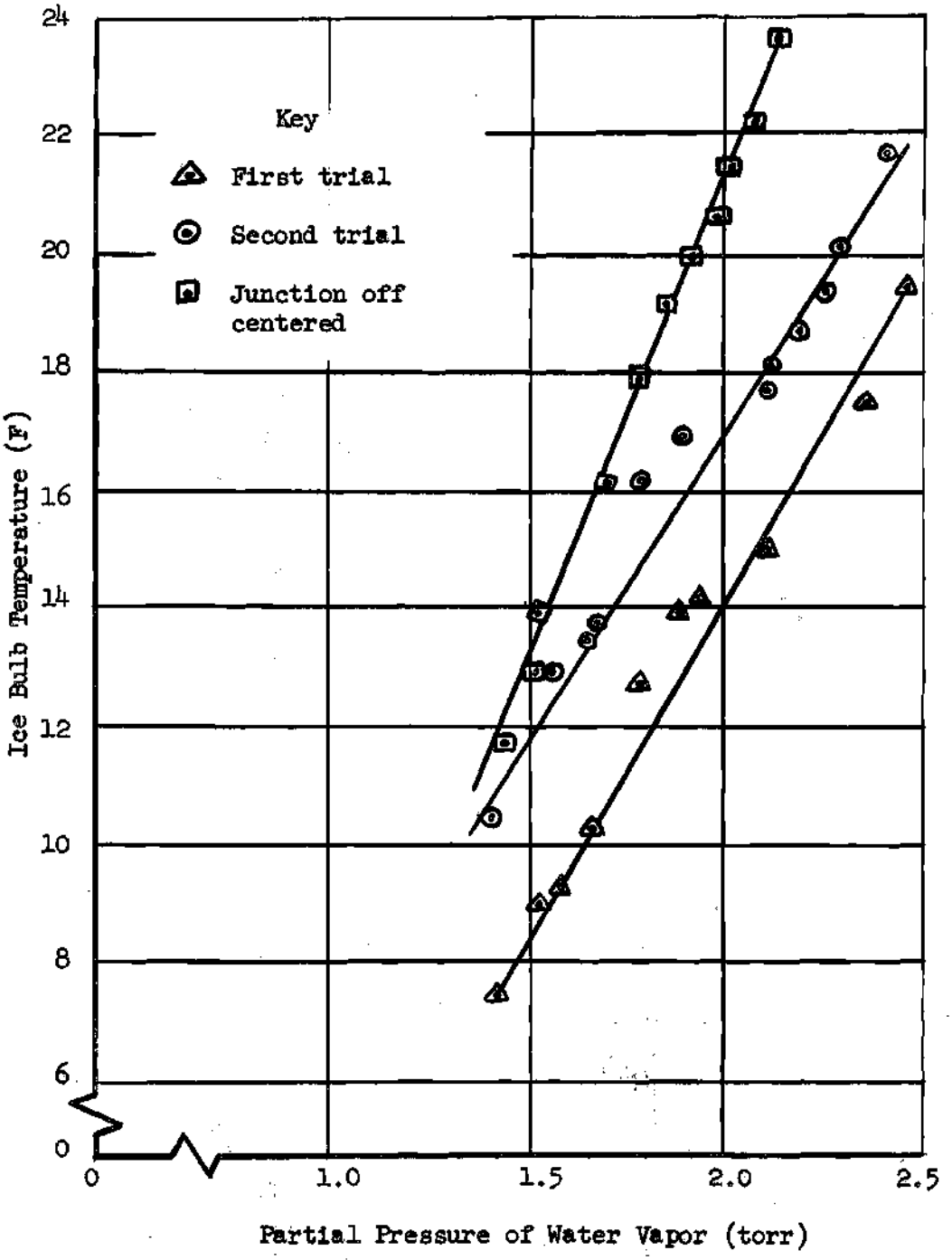


Figure 11. Ice Bulb Calibration Attempt
(diameter = .45 inches, P_T = 3.0 torr)

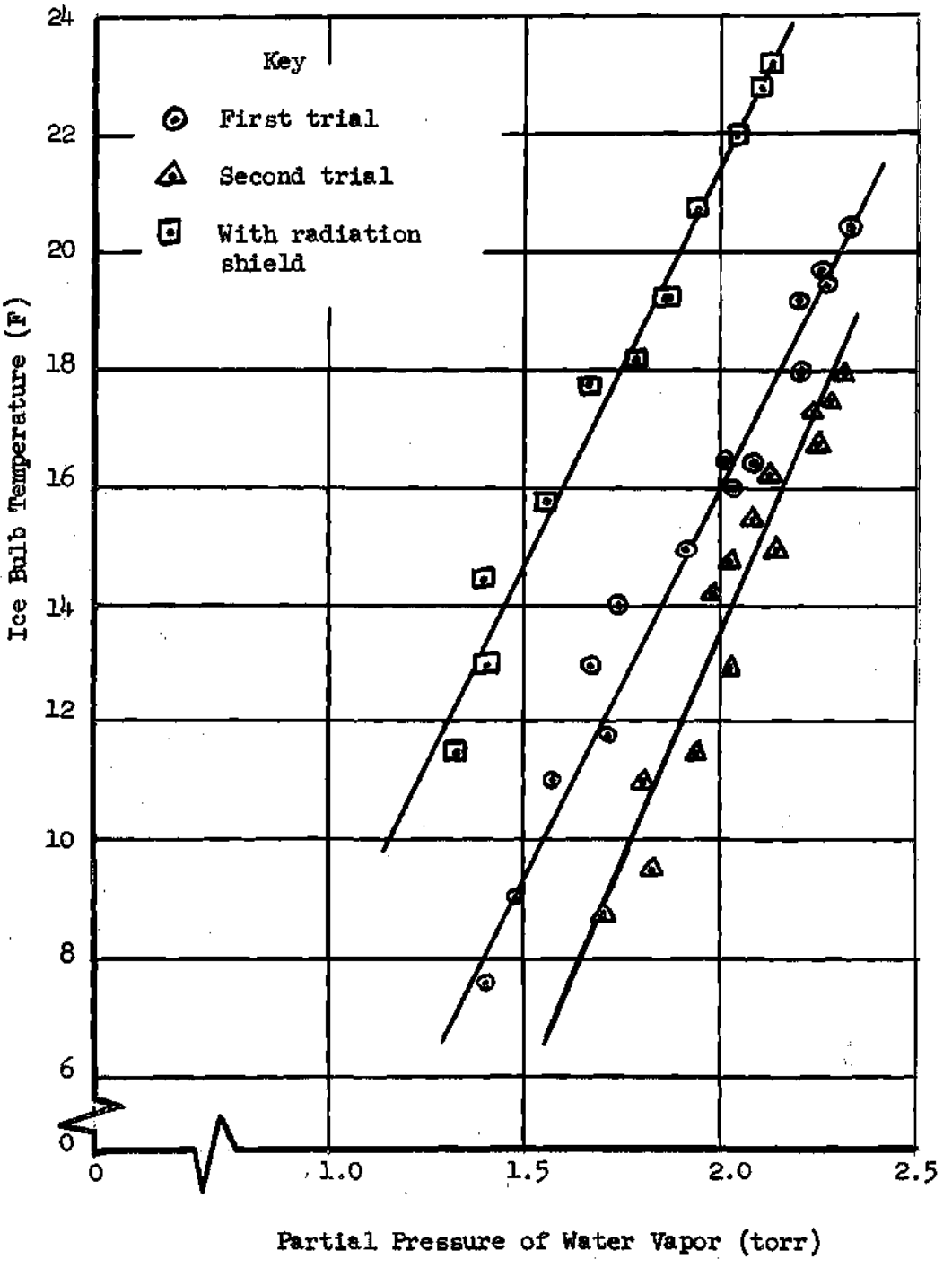


Figure 12. Ice Bulb Calibration Attempt
(diameter = .75 inches, P_T = 3.0 torr)

An experiment was run to check the feasibility of the latter explanation. An ice bulb was prepared with the thermocouple junction purposely positioned close to the surface of the ice. The results of this run are plotted in Figure 11. When the system was initially pumped down and still at low humidity, the off center thermocouple read temperatures nearly the same as the centered thermocouples. As the subliming ice caused the humidity to rise, the temperature increase was considerably faster than that experienced for the centered thermocouples. This indicates that a uniform ice temperature was not reached.

The above results show that complete ice bulb equilibrium is necessary for an accurate evaluation. A steady flow situation would permit the sample to be held in a constant pressure and humidity environment. The ice would then attain a uniform temperature. Presently available equipment does not provide a means to obtain this desired steady flow.

An additional run was made to note the effect of a radiation shield on the ice bulb temperature. A cylinder of aluminum foil was suspended around the large diameter ice bulb to serve as a radiation shield. The calibration resulting from this situation is shown in Figure 12. The graph shows an essentially constant difference between the temperatures of the shielded and unshielded ice bulbs. Increased water vapor content within the radiation shield could have caused such a result. The electrical transducer would have read humidities somewhat lower than those actually surrounding the ice bulb.

The Gas Analysis

The graph in Figure 13 shows the results obtained with the gas analysis equipment. The equipment definitely indicates the water vapor content of the mixture but considerable scatter is experienced. The scatter is probably a result of difficulty in matching the fluid levels within the burette and leveling bulb. Only a small pressure differential existed across the fluid and matching the levels could not be accomplished with the desired sensitivity. Operation of the analyzer was investigated at pressures near 6 torr. At pressures lower than this, extreme difficulty was experienced in matching the fluid levels and consistent data could not be obtained.

Use of a desiccant is definitely possible for analyzing low vacuum air-water vapor mixtures. However, to reach pressures lower than 6 torr, a more sensitive means of applying the desiccant is necessary.

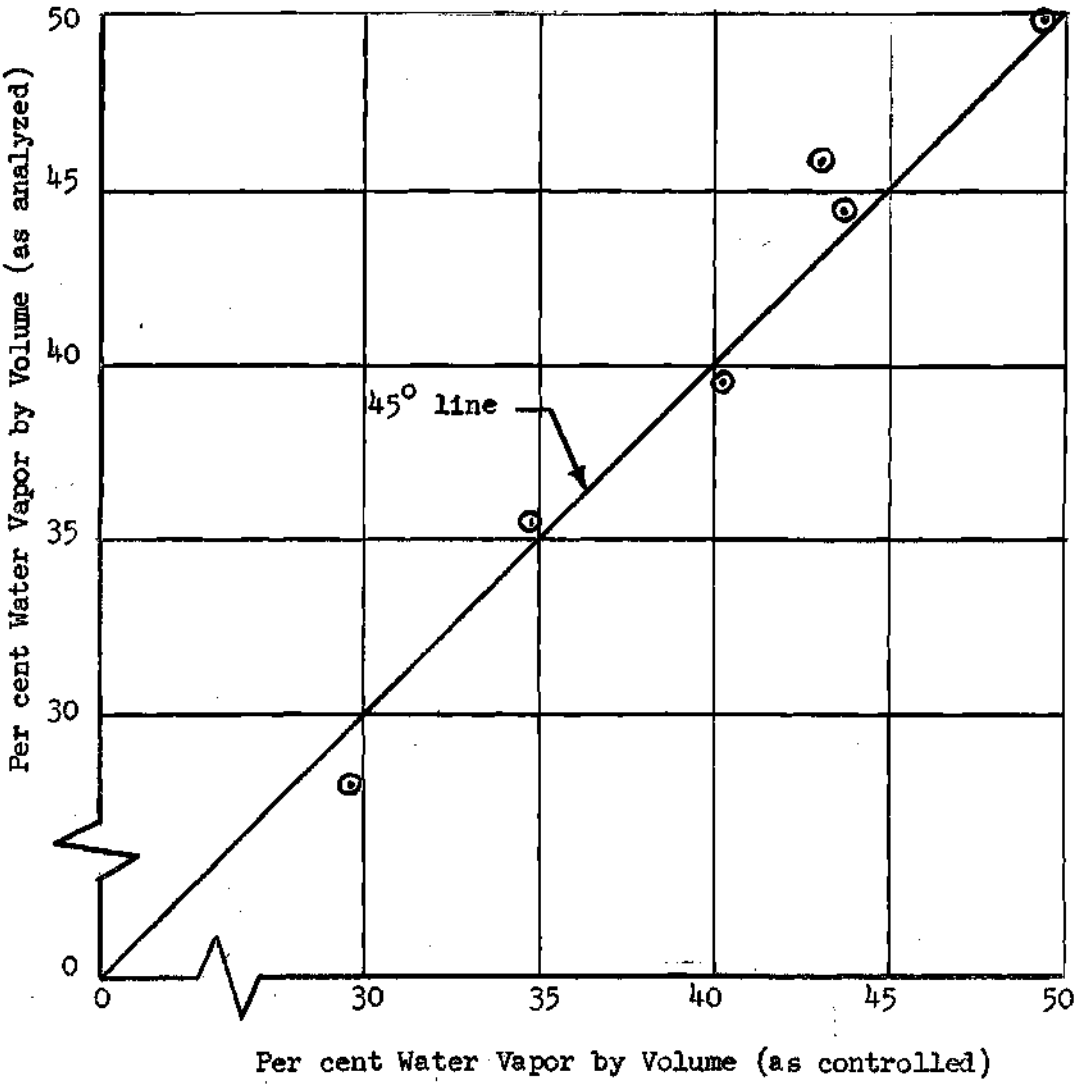


Figure 13. Results of the Gas Analysis versus Controlled Water Vapor Content

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this investigation was to determine a convenient means for analyzing air-water vapor mixtures under low vacuum conditions. The investigation of four methods for analyzing air-water vapor mixtures under low vacuum conditions -- an electrical hygrometer, a liquid nitrogen cold trap, an ice bulb thermocouple and a gas analyzer -- resulted in the following conclusions:

1. The electrical hygrometers used can be employed to measure humidity at low vacuum pressures. Three transducers (model numbers 4-4812, 4-4814 and 4-4815) were investigated at pressures as low as .5 torr. The transducers responded only to the temperature and the partial pressure of water vapor in their surrounding environment. Calibration curves supplied by the manufacturer were found to be accurate within 5 per cent.

2. Previous work (9) has shown that when a liquid nitrogen cold trap is placed in an air-water vapor mixture at a total pressure below 100 microns, the pressure measured at the cold trap is equal to the partial pressure of air in the mixture. This investigation shows that for pressures between .4 and 3.2 torr, the cold trap pressure and total pressure are indistinguishable.

3. The temperature read by an ice bulb thermocouple is sensitive to the water vapor content of a low vacuum air-water mixture.

Satisfactory equilibrium conditions could not be reached with the existing equipment. This prevented the successful development of a calibration curve.

4. A gas analyzer, with a silica gel desiccant, can be used to measure the partial volume of water vapor in a low pressure air-water vapor mixture. A lack of sensitivity in the present method of application limited operation to pressures above 6 torr and resulted in errors up to 10 per cent.

As a result of this investigation, further work in the area of low vacuum air-water vapor mixtures may be recommended:

1. A sensitive differential pressure gage should be used to compare more accurately the total mixture pressure to the pressure measured at the cold trap.

2. Measurement of ice bulb temperatures in the steady flow of a known air-water vapor mixture should allow the development of an accurate ice bulb calibration curve. Equilibrium could be obtained in spite of the subliming ice.

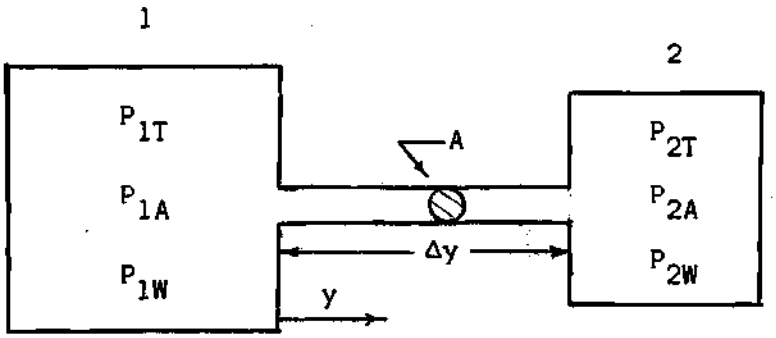
3. A more sensitive method for applying the silica gel desiccant should result in satisfactory results at pressures lower than the 6 torr investigated here.

APPENDIX A

TIME DEPENDENCE IN COMBINING MIXTURES

When applying the laboratory standard, it was important to have mixtures of equal concentration in each tank shown in Figure 2. An analysis was conducted to investigate the effect of having unequal concentrations in the tanks. The rate at which these mixtures would approach an equilibrium condition was studied.

In Figure 14, two tanks are shown connected in much the same manner as those in Figure 2. At time zero, both tanks contain air-water vapor mixtures of equal pressure. However, tank 1 contains



$$P_{1T} = P_{2T}$$

$$P_{1W} > P_{2W}$$

Figure 14. Analytical Model of the Laboratory Standard.

more water vapor than tank 2. The progress of this system toward equilibrium will now be investigated.

Water vapor flows from tank 1 into tank 2 (and air in the opposite

direction). This flow takes place due to one-dimensional molecular diffusion. The governing equation can be written in the form

$$\frac{\dot{m}_W}{A} = \frac{-D_v}{RT} \frac{P_{2W} - P_{1W}}{y_2 - y_1} \tag{A.1}$$

An expression for the partial pressure of water can be written for each tank at any instant of time. If a perfect gas is assumed, the transient partial pressure of water vapor in tanks 1 and 2 is given by

$$(P_{1W})_t = (P_{1W})_{t=0} - \frac{RT}{V_1/m_W} \tag{A.2}$$

$$(P_{2W})_t = (P_{2W})_{t=0} + \frac{RT}{V_2/m_W} \tag{A.3}$$

respectively. The term m_W refers to the mass of water vapor which has been transferred from tank 1 to tank 2 since the instant of zero time.

The expression for the difference in water vapor partial pressures at any time can now be written by combining equations (A.2) and (A.3),

$$(\Delta P_w)_t = (P_{1W})_t - (P_{2W})_t = (\Delta P_W)_{t=0} - RT\left(\frac{1}{V_1} + \frac{1}{V_2}\right) m_W \tag{A.4}$$

Differentiating equation (A.4) with respect to time and rearranging gives

$$\dot{m}_W = \frac{-1}{RT\left(\frac{1}{V_1} + \frac{1}{V_2}\right)} \frac{d(\Delta P_W)_t}{dt} \tag{A.5}$$

Equations (A.5) and (A.1) can be combined and simplified to yield,

$$\frac{d(\Delta P_w)_t}{dt} + \frac{D_v A(\frac{1}{V_1} + \frac{1}{V_2})}{\Delta y} (\Delta P_w)_t = 0 \qquad (A.6)$$

The solution of equation (A.6) may be written as

$$(\Delta P_w)_t = C\, e^{-t/\tau} \qquad (A.7)$$

where

$$\tau = \frac{\Delta y}{D_v A(\frac{1}{V_1} + \frac{1}{V_2})} \qquad (A.8)$$

The constant, C, can be evaluated at time zero. The final solution to equation (A.6) becomes

$$(\Delta P_w)_t = (\Delta P_w)_{t=0}\, e^{-t/\tau} \qquad (A.9)$$

The time constant, τ, represents the time required for the difference in the partial pressures to reach 37 per cent of the original difference. The time constant can be evaluated for the equipment shown in Figure 2. The following values may be assumed:

$$A = .00306 \text{ ft}^2$$

$$V_2 = .204 \text{ ft}^3$$

$$V_1 = 1.60 \text{ ft}^3$$

$$\Delta y = 3 \text{ ft}$$

$$P_{1T} = P_{2T} = 4 \text{ torr} = .0768 \text{ psia}$$

$$T = 80\,F = 540\,R$$

The mass diffusivity constant can be calculated from the following equation (3):

$$D_v = .892 \frac{P_o}{P} \left(\frac{T}{T_o}\right)^{1.81} \qquad (A.10)$$

Substituting the appropriate values in equation (A.10) gives $D_v = 222$ ft^2/hr. Equation (A.8) can now be solved for the time constant, thus $\tau = .8$ hours.

A time of .8 hours is certainly appreciable. The analysis therefore indicates that mixtures of equal concentration should be set up in both tanks to achieve accurate results. Such a procedure was followed in applying the laboratory standard.

APPENDIX B

A CHANGE IN THE TRANSDUCER CALIBRATION

In the course of the experimental work, the low range humidity transducer (element 4-4812) shifted from its original calibration curve. The new calibration and the original curve are plotted in Figure 15.

The calibration change was noted after an experimental error allowed a mist of Dow Corning silicone fluid to be sprayed into the tank containing the humidity transducer. It is felt that a contamination of the sensing element occurred which changed its response to surrounding humidities. This calibration shift shows that care must be taken in the use of these sensitive elements. As mentioned by the manufacturer, exposure to certain chemicals can cause a change in the transducer calibration.

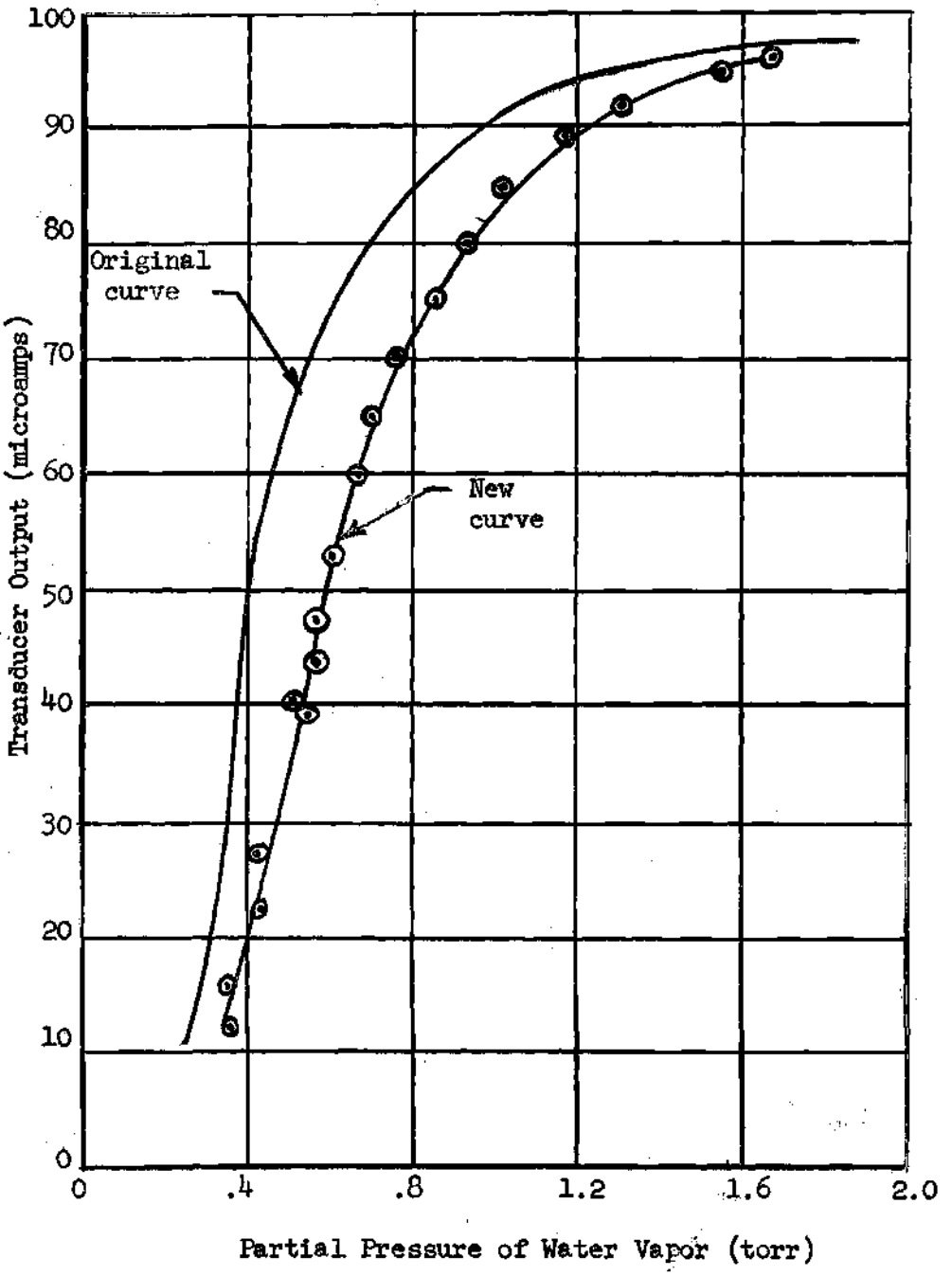


Figure 15. A Shift in Calibration
(Element 4-4812, T = 80 F)

LITERATURE CITED

1. E. F. Obert, Concepts of Thermodynamics, New York: McGraw-Hill Book Co., (1960) pp. 312-356.

2. G. J. Van Wylen, Thermodynamics, New York: John Wiley and Sons, Inc., (1959) pp. 203-228.

3. E. R. G. Eckert and Drake, Heat and Mass Transfer, second edition, New York: McGraw-Hill Book Co., (1959) pp. 439-478.

4. F. Kreith, Principles of Heat Transfer, Scranton, Pennsylvania: International Textbook Company, (1958) pp. 489-519.

5. W. Schaeffer, "Simple Theory of the Electric Hygrometer," Journal of the American Meteorological Society, Vol. 27 (1946), pp. 147-151.

6. V. B. Moris and F. Sobel, "Some Experiments on the Speed of Response of an Electrolytic Hygrometer," Journal of the American Meteorological Society, Vol. 35 (1954), pp. 226-229.

7. A. Wexler, et al., "A Fast Responding Electric Hygrometer," Journal of Research, U. S. National Bureau of Standards, Vol. 55 (1955), pp. 71-78.

8. M. J. Sienko and R. A. Plane, Chemistry, second edition, New York: McGraw-Hill Book Co., (1961) p. 211.

9. C. H. Stallings and D. H. Martin, "Investigation of Air and Water Vapor Pressures in a Five and Six Stage Steam Jet Ejector," Vacuum Symposium Transactions, (1963) pp. 297-300.

10. D. F. Dyer, Measurement of Water Vapor Content of Air-Water Vapor Mixtures at Low Vacuum Pressures, M. S. Thesis, Georgia Institute of Technology (1964).

11. W. C. Thuman and E. Robinson, "Determination of Humidity at Temperatures Below Freezing," Journal of Meteorology, Vol. 11 (1954), pp. 214-219.

12. J. A. Goff and S. Gratch, "Low Pressure Properties of H_2O From -120F to 212F," Heating, Piping and Air Conditioning, Vol. 18, (1946) pp. 125-136.

13. V. E. Suomi, "Moisture Measurement with an Electronic Dew Point Indicator," Instruments, Vol. 21 (1948), pp. 178-182.

14. S. H. Jury and W. Licht, "An Automatic Frost Point Hygrometer," Analytical Chemistry, Vol. 22 (1950, pp. 1536-1540.

15. B. N. Clack, "An Electrical Method of Measuring Water Vapor Pressure in a Sealed Off Discharge Tube," Journal of Scientific Instruments, Vol. 26 (1949), pp. 58-59.

16. O. G. Griffin and C. M. Stringfield, "A Dew Point Meter Based on Thermoelectric Cooling," Journal of Scientific Instruments, Vol. 41 (1964), p. 241.

17. D. F. Dyer and J. E. Sunderland, "A Standard for Vapor Pressure Measurements at Low Pressures," To appear in Vacuum, 1964.

18. F. W. Dunmore, "An Improved Electric Hygrometer," Journal of Research, U. S. National Bureau of Standards, Vol. 23 (1939), pp. 701-714.